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# Miniature time-of-flight mass spectrometers for in situ composition studies

W.B. Brinckerhoff\*, T.J. Cornish, R.W. McEntire, A.F. Cheng, R.C. Benson

*The Johns Hopkins University, Applied Physics Laboratory, 11100 Johns Hopkins Road, Laurel, MD 20723, USA*

## Abstract

We present a description of and results from our ongoing development of miniature time-of-flight mass spectrometers (TOF-MS) for future landed planetary missions. A new, flexible TOF-MS instrument has been developed to permit the analysis of elemental, isotopic, and molecular composition in solid samples. The new instrument incorporates normal-incidence ultraviolet pulsed laser desorption, a gridless ion source, and a novel curved-field reflectron to maximize sensitivity and resolution over wide abundance and mass ranges. Results with unprepared sample materials are compared with previous work based on infrared laser ablation. Flight instruments based on these technologies can potentially be as small as a soda can without sacrificing their ability to detect low levels of atomic and organic species at grain scales.

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## 1. Introduction

Small-scale planetary missions are now taking a dominant position in our plans to explore the solar system. As initial rendezvous and reconnaissance-type missions to major targets are completed, we will be looking for technologies that enable the *landed* study of a variety of bodies in greater depth. New science priorities will develop that can only be addressed by long-stay surface missions on multiple small bodies, moons, Mars, Mercury, etc. Both in situ measurements and sample return will be required.

On such extensive surface missions, the composition of solid materials from various locations and depths will be the primary goal. The elemental and mineralogical analysis of rocks, soils, etc. will be used

to determine geological context and make comparisons to chondritic or other meteoritic compositions. Several instruments to achieve this goal have been developed. However, there are certain measurements that are considered the most significant, and the most difficult, for any robotic probe. These include: (1) measurement of isotope systematics in key low-mass elements such as H, C, O, N, and S; (2) detection of trace levels of rare earth elements within individual mineral grains inside bulk rock; (3) quantitative measurement of radiogenic isotopes at the part-per-billion levels for age dating; and (4) trace detection of moderate to large organic molecules in sedimentary deposits and ices [1].

These measurements are currently achieved only with large equipment in terrestrial laboratories. The main instrument used is the ion mass spectrometer, with electron or ion beams, or multiple, high-power lasers. The resources required have heretofore precluded such detailed measurements with robotic in situ probes. However, miniaturized laser technology and

\* Corresponding author.

E-mail address: [will.brinckerhoff@jhuapl.edu](mailto:will.brinckerhoff@jhuapl.edu)  
(W.B. Brinckerhoff).

ultra-short ion flight tube designs are now enabling the development of highly capable mass spectrometers for flight. It is not unreasonable to speculate that these critical measurements could one day be made robotically by instrument suites including miniature mass spectrometers.

We present results from our miniature laser time-of-flight mass spectrometer (TOF-MS) development that begin to address some of the broad-band and high-sensitivity goals of future landed missions.

## 2. IR laser ablation TOF-MS

Previous work with a laser ablation mass spectrometer (LAMS) [2–5] has demonstrated that semi-quantitative elemental and isotopic analyses of unprepared rock specimens can be obtained with a 1064 nm Q-switched Nd:YAG laser focused to  $10^9 \text{ W cm}^{-2}$ , in a TOF-MS less than 20 cm in length. Such high irradiance produces a large flux of prompt atomic ions (and essentially no molecular species). Ion pre-acceleration was not used, as the kinetic energies (up to 250 eV) were focused and windowed. A coaxial two-stage reflectron provided a resolution of  $R = m/\Delta m > 250$  (FWHM). This was sufficient to separate singly-charged unit-mass peaks up to 250 amu, giving chemical analyses (abundance ratios to within 10–15% and isotopes to within 5–7%) within a few laser shots. Precision of Mg, Al, S, Ca, and Fe ratios to Si permitted differentiation between chondrite classes [2,3].

A single laser shot LAMS spectrum from a CM2 carbonaceous chondrite is shown in Fig. 1. The energy window used for this spectrum was 120–150 eV. Integrated peak areas are related to the atomic percentage of the particular isotope in the ablated plume. An intrinsic bias evident in single shot spectra arises from the varying kinetic energy distributions of ablated elements. This effect can be calibrated to some degree by determining the relative sensitivities of different elements over a range of energy windows. In addition, each focused laser shot samples a microscopic area ( $< 50 \mu\text{m}$  diameter), to probe individual mineral grains. Such analyses can provide crucial support for mineralogical classification. Bulk analyses can be achieved by averaging over multiple shots and/or defocusing the laser.

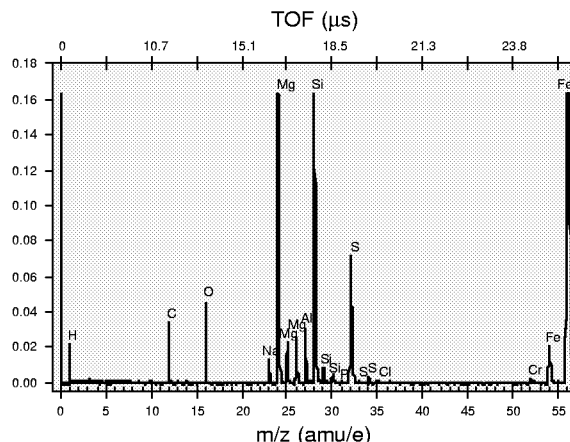


Fig. 1. Single laser shot LAMS spectrum of a CM2 chondrite. Laser pulse width is 8 ns. Energy pass window is (120,150) eV.

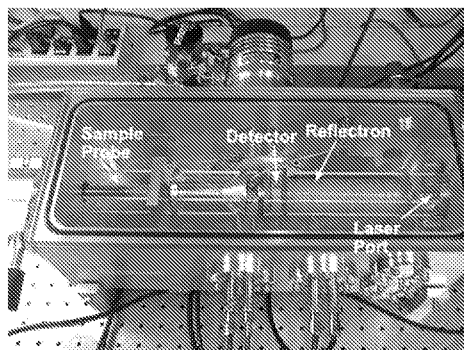


Fig. 2. Miniature laser TOF-MS prototype and test chamber, with coaxial desorption, gridless extraction, and curved-potential reflectron.

## 3. UV laser desorption TOF-MS

We have built a new laser TOF-MS instrument (Fig. 2) to address some of the limitations of LAMS and to investigate new capabilities for organic/molecular detection and trace analysis in extraterrestrial rocks, soils, and ices. Our goal is to increase the performance of miniature TOF-MS without incurring significant mass, power, or complexity increases. The basic prototype testbed comprises a vacuum chamber with various electrical and optical ports. The chamber pressure is maintained at  $10^{-7}$  Torr. The flight tube is mounted on ceramic rods

along the long axis of the chamber, so that the laser enters coaxially from one end and focuses to the sample on a feedthrough at the other end. The chamber is longer than the mass spectrometer itself, to permit various configurations to be tested easily. A 5–7 ns pulse from a compact Q-switched Nd:YAG laser is used at its fundamental wavelength (1064 nm) or frequency tripled (355 nm) or quadrupled (266 nm) with harmonic crystals. The beam is expanded with a plano-concave singlet, attenuated to an energy between 0 and 3 mJ with a variable filter, and focused through a quartz viewport with an achromatic doublet. The laser is coupled into the optical axis with a 45° notch mirror (i.e., for the chosen wavelength). A CCD camera can view the sample through the mirror and objective. At focal lengths of 30–40 cm, the 355 nm laser spot diameter can be as small as 30  $\mu\text{m}$  RMS. Irradiances up to several  $\text{GW cm}^{-2}$  can be attained, however we normally operate with the laser highly attenuated ( $10^6$ – $10^7 \text{ W cm}^{-2}$ ).

The current TOF-MS length and diameter are 20 and 5 cm, respectively. The technique is directly scalable to smaller sizes, and a new half-size prototype is being designed. The following improvements have been addressed with the new instrument:

### 3.1. Ideal reflectron

Ablation produces ions with energies up to hundreds of eV. The reflectron voltage  $V_R$  sets a high-energy cut-off on this distribution (whether it is shifted by source extraction or not). A two stage reflectron temporally focuses the range above  $\sim 0.8V_R$  with unit mass resolution. Ions below this range are rejected by a barrier grid in front of the detector. As this energy window samples only a fraction of the total distribution, the reflectron voltage must be scanned over a set of values to obtain statistically meaningful abundances. However, the number of laser shots available for this procedure may be limited by the power budget and the need to interrogate individual mineral grains.

An alternative approach is to focus a wider range of energies with a higher-order reflectron. We are using novel curved-potential reflectrons [6] that provide nearly ideal focusing over a much higher fraction (up to 90%) of ion energies, for either ablation or desorption. The reflectrons comprise a sequence of metal-

lic ring electrodes deposited along the inner-surface of a lightweight fiberglass tube (Fig. 2). This simple method has permitted us to analyze various ways to achieve the optimal potential profile. In one design, the rings are equally spaced along the tube, with varying resistance steps. In an alternate design, the rings are variably-spaced, with fixed resistance steps. This latter design may enable optimal tuning of the flight times of higher-energy (primarily atomic) ions, while simultaneously focusing higher-mass molecular species. The need for scanning is thus reduced both for capturing the abundances of individual species and for detecting atomic and molecular species in each laser shot.

### 3.2. High transmission efficiency

Achieving high sensitivities, especially to detect trace atoms and molecules, is critically dependent on maximizing the fraction of ions that reach the detector. The ion transmission in LAMS [5], approximately  $10^{-6}$ – $10^{-5}$ , was due to the inlet aperture stop ( $10^{-3}$ ), energy windowing ( $10^{-2}$ – $10^{-1}$ ), and the cumulative grid transparency ( $10^{-1}$ ). The new reflectron design eliminates much of the latter two limitations. To maximize transmission through the inlet (a center hole in the detector assembly), we are using a novel gridless source that accelerates and collimates ions leaving an unprepared sample surface.

There are certain trade-offs in going to a design with an ion source. The gap between sample and instrument must be small (a few mm); ideally, a rock chip would be robotically acquired and positioned with a precision manipulator. Further, the inlet elements must be set to a fixed, moderate (negative) voltage relative to the sample. At ablation irradiances, such as used in LAMS ( $\sim 10^9 \text{ W cm}^{-2}$ ), a high-density plasma is formed above the sample that would severely disturb the intended effect of the source field via electromagnetic shielding. Spark breakdown discharges in the source are readily observed at high irradiances with a few kV potential drop. Therefore, desorption-level irradiances ( $< 10^8 \text{ W cm}^{-2}$ ) are primarily used instead of ablation. While fewer particles are produced in this range, the ion source efficiently transfers nearly all ions formed into the reflectron, giving a critical sensitivity boost. This ion “extraction” also increases mass resolution, by narrowing the ion energy spread relative to the mean energy.

### 3.3. Improved ionization efficiency

The sensitivity is also directly affected by the production of atomic and molecular ions from the sample surface. We are using an ultraviolet (UV) pulsed laser (266 and 355 nm Nd:YAG harmonics) which focuses to a smaller spot and couples more efficiently to heterogeneous samples than IR wavelengths [7,8]. In the lower irradiance range used, the reduced absorbance fractionation of UV among minerals is important for low-level, grain-to-grain analyses. UV photons also ionize neutral atoms and molecules more efficiently in the desorption range than IR. In particular, many organic molecular species with masses up to 1000 amu are readily desorbed and ionized with the UV laser without chemical sample preparation [9]. This mass range covers biomolecular species, such as nucleosides, PAHs, amino acids, some peptides, and lipids, which can be probed on a shot-by-shot basis. When combined with the elemental and isotopic data from the same spectrum, UV desorption of organics may provide a valuable tool in the search for samples of astrobiological interest.

To enable trace detection, we are also working with a miniaturized postionization system using a tunable laser. In the irradiance range  $10^5$ – $10^6$  W cm<sup>-2</sup>, few prompt ions are formed; desorbed species are predominantly neutral, and can be emitted over several microseconds. By carefully timing a second laser pulse to overlap the neutral cloud above the sample, highly

sensitive and selective multiphoton ionization experiments may be performed. The wavelength is selected to match a metastable excited line, or closely-spaced multiplet, particular to a molecule of interest, effecting a simple form of resonance ionization spectroscopy (RIS) [10]. Even with a relatively simple two-laser scheme, efficiency can be enhanced by several orders of magnitude over prompt ionization [10,11]. With an eye toward potentially space-qualifiable technology, we have coupled a small optical parametric oscillator (OPO) and timing circuit into the TOF-MS. The wavelength range of near-UV through visible covers pertinent cyclic hydrocarbons, major rock-forming elements, and rare earths [11,12].

### 4. Results

We have tested the basic UV direct desorption mode of the new instrument with a range of simple samples. No special sample handling precautions were taken; a small amount of surface salt contamination was burned away in a few dozen laser shots at moderate irradiance, after which spectra were remarkably reproducible.

A single-shot spectrum, with a 10 cm long, equally-spaced reflectron, from a Pb solder foil target is shown in Fig. 3. The laser wavelength was 355 nm Pb isotopes at  $m/z$  204, 206, 207, and 208 were baseline resolved; the mass resolution was near 1000 (FWHM). Signals observed slightly delayed from

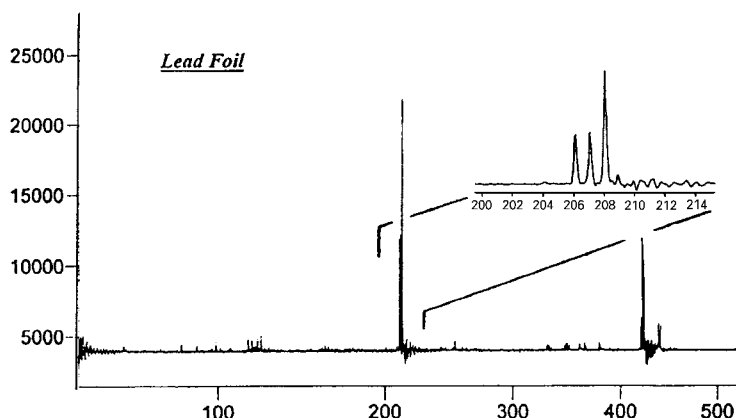


Fig. 3. Single shot UV (355 nm) direct desorption mass spectrum from a Pb solder target. Surface also contained residual ink sample deposited for combined analysis.

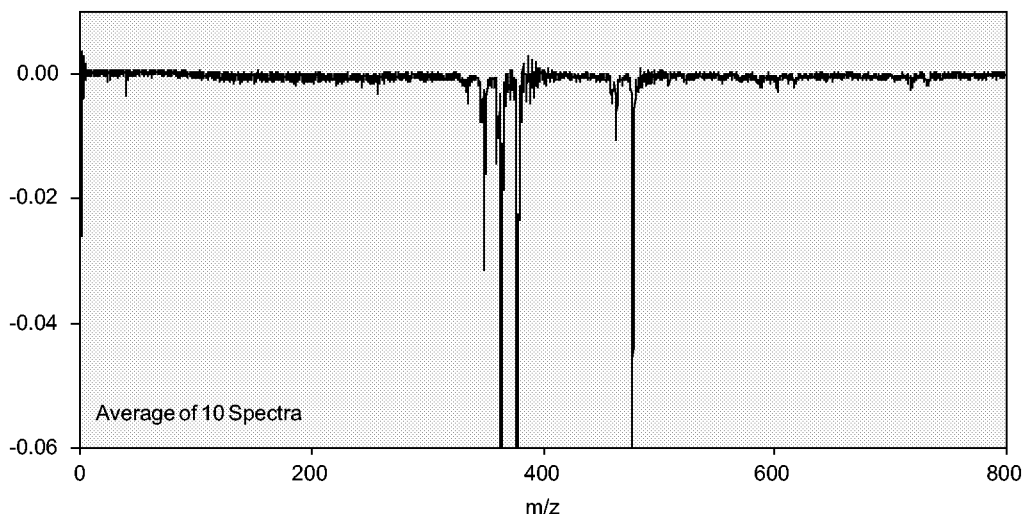


Fig. 4. UV direct desorption mass spectrum (10 laser shots) of blue pen ink applied to probe tip.

each peak arose from detector response and may be suppressed; peak widths were limited by the 5–7 ns laser pulse. This represents a significant achievement for such a small instrument.

A 120-shot average (10 Hz at 355 nm) from this target retained high resolution, due to low TOF jitter, while signal-to-noise was dramatically increased. A very simple Gaussian peak fit and baseline subtraction yielded isotopic abundances within 5% of standard values for Ag and Pb.

The mass range has been checked with a series of organic compounds dried from solution on the probe tip. We initially tuned the reflectrons with MALDI targets, demonstrating a detectable range of thousands of amu. However, unprepared samples are the main focus for in situ applications. A simple blue ink pigment was readily ionized (Fig. 4) and demonstrates the ability to detect intact molecular structures in the range below 1000 amu. This ink sample was also applied to the lead foil surface. Fig. 3 demonstrates the ability to obtain single-shot isotopically-resolved elemental and organic/molecular spectra with direct UV laser desorption.

## 5. Applications

The increased sensitivity of the UV TOF-MS to organic compounds, coupled with its ability to probe

composition with fine lateral (30  $\mu\text{m}$ ) and depth ( $< 0.1 \mu\text{m}$ ) resolution, is very encouraging for in situ planetary exploration potential. Incorporating these capabilities into an instrument that works with unprepared solid samples enables both survey and in-depth analyses, depending on the requirements and mobility of the mission.

Micro-focused laser TOFMS can play an important role in mineralogical analyses. While bulk measurements, such as obtained with APXS and X/GRS instruments, can provide important insights into the mineralogy of a planetary object, they are not capable of directly detecting individual minerals. For example, the S-free rock composition determined by the Mars Pathfinder APXS [13] is similar to that of the volcanic rock andesite. High spatial resolution measurements of the mineralogy and composition of these rocks would greatly increase our understanding of their origins. At the scales probed by laser TOF-MS, elemental and molecular composition is diagnostic of mineralogy, and can provide rapid analyses that calibrate and complement in situ XRD/XRF data. By creating surface element maps at the scale of grains, TOF-MS can reveal the probable identity of grains and the relationship to other grains, constraining the range of formation mechanisms of the sample rock.

The microprobe capability is also extremely important for grain-scale detection of organic molecules, particularly in carbonaceous material on small

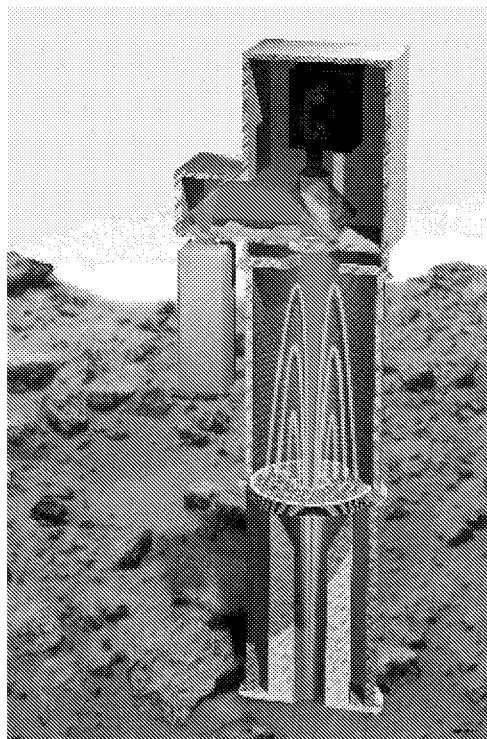


Fig. 5. Laser TOF-MS with curved-field reflectron and co-focused laser and imager.

bodies and in aqueously altered deposits on Mars. Generally, the organic inventory on a small body is of interest for pre-biotic chemistry and the delivery of primitive material to/within the solar system. It is presumed that the most primitive bodies are quite homogeneous on the 100  $\mu\text{m}$  scale, but no landed in situ measurement has been made. The detected presence of mixed CHON and silicate particles in cometary comae [14] is strongly indicative of the presence of refractory organics, including large unsaturated hydrocarbon polymers, in cometary nuclei. The distribution of organics in Mars rocks and soil deposits is likely to be highly heterogeneous, so a microprobe with both sensitivity and mass range would be a key capability there as well. A schematic drawing of a Mars laser TOF-MS is shown in Fig. 5. Conspicuously absent from this figure are the sampling and vacuum systems. The weight and power requirements of sample manipulators and vacuum pumps have in the past been a major barrier to designing high-sensitivity

landed mass spectrometers for bodies with significant atmospheres (Mars, Venus, Titan, etc.) Recent developments at JHU/APL and elsewhere have begun to lower these barriers, potentially bringing the *total* package mass and power draw to well below 5 kg and 10 W, respectively.

For both atomic and organic/molecular analysis, the next step beyond current capabilities is to significantly lower detection and determination limits. Much more definitive science can be obtained with a one-to-two order increase in average signal-to-noise in grain-focused laser shots. Simple RIS-based in situ laser analyses may enable this increase without demanding extensive sample preparation steps. Solid-state tunable-laser ionization can selectively increase the sensitivity to key minor and trace species. Several rare earth and other elements occur at 0.01–10 ppm-weight bulk abundances in meteorites (Table 1). Those that have single-color (1 + 1) resonance ionization schemes in the near-UV and visible wavelengths can be ionized with a very modest Nd:YAG-pumped OPO. We are currently testing the ability of the TOF-MS microprobe to find grains containing higher than average quantities of key rare earth and organic species. A two-step resonant ionization analysis of those grains may enable, for example, detection of a Europium anomaly or correlations of Lanthanides with elements such as Ca and Ti.

The tunable laser TOF-MS development particularly addresses long-term goals 2 and 4 mentioned in the Introduction. TOF-MS may eventually also form an important part of a system capable of achieving the isotope ratio systematics goals (1 and 3). However, it may be that the much higher sensitivities and precision required for quantifying small isotope fluctuations can only be attained with careful sample preparation, internal standardization, and extremely reproducible ionization methods. At present, these analyses are beyond what can be accomplished robotically, at least on a low-cost planetary mission. Further development of the laser microprobe technique is needed, including advances in tunable diode lasers and OPOs, resolution of calibration issues, such as the laser ionization bias of odd vs. even isotopes, and novel robotic sample preparation methods. Eventually, very small landed science packages and mobility systems may (respectfully) acquire some of the capabilities of

Table 1

Abundance and spectroscopic data for selected trace elements in CI and Nakhla meteorites. RIS wavelength data compiled from Refs. [15–17]

Elt.	Z	CI (ppmw)	Nakhla (ppmw)	IP (eV)	$\lambda[\omega 1 + \omega 1]$ (nm)
Ga	31	9.8	3.0	6.00	287.42
Ge	32	33.0	3.0	7.90	259–276
Rb	37	2.3	3.8	4.18	358.7
Sr	38	7.3	59.0	5.70	460.7
Y	39	1.56	3.3	6.38	291.9
Nb	41	0.25	1.6	6.88	408
Mo	42	0.92	0.086	7.10	313.3
Cs	55	0.19	0.390	3.89	455.53
Ba	56	2.35	29.0	5.21	553.7
La	57	0.235	2.06	5.58	441.4
Ce	58	0.62	5.87	5.54	436.4
Nd	60	0.46	3.23	5.53	438.2
Sm	62	0.15	0.77	5.64	436.6
Eu	63	0.057	0.24	5.67	446.8
Gd	64	0.200	0.86	6.15	447.6
Tb	65	0.037	0.12	5.86	432.6
Dy	66	0.250	0.77	5.94	433.5
Ho	67	0.056	0.155	6.02	410.4
Er	68	0.160	0.37	6.10	400.8
Tm	69	0.025	0.047	6.18	371.8
Yb	70	0.160	0.39	6.25	398.8
Lu	71	0.025	0.055	5.43	451.9
Hf	72	0.105	0.27	6.65	368.2
Ir	77	0.465	0.000	9.10	285.0
Pb	82	2.50		7.42	283.31

geologists and geochemists, and provide a new level of in situ analyses to complement sample return and piloted missions.

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